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Microbiologically Influenced Corrosion of Corrosion Resistant Materials

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Abstract

The corrosion resistance of materials cannot be accurately determined in abiotic electrolytes. Field and laboratory studies document microbiologically influenced corrosion (MIC) of corrosion resistant materials including copper and nickel alloys, stainless steels containing 6% molybdenum and polymeric composites.

Discussion

Microbial biofilms develop on all surfaces in contact with aqueous environments. Chemical and electrochemical characteristics of the substratum influence formation rate and cell distribution of microfouling films during the first hours of exposure. Electrolyte concentration, pH, organic and inorganic ions also affect microbial settlement. Biofilms produce an environment at the biofilm/surface interface that is radically different from that of the bulk medium in terms of pH, dissolved oxygen, and inorganic and organic species. Reactions within biofilms can control corrosion rates and mechanisms. The term microbiologically influenced corrosion (MIC) is used to designate corrosion resulting from the presence and activities of microorganisms within biofilms. Reactions are usually localized and can include: 1) sulfide production, 2) acid production, 3) ammonia production, 4) metal deposition, 5) metal oxidation/reduction and (6) gas production.

Copper Alloys

Copper alloys are frequently used for seawater piping systems and heat exchangers due to their good corrosion resistance combined with mechanical workability, excellent electrical and thermal conductivity, ease of soldering and brazing, and resistance to macrofouling. In oxygenated seawater a film of cuprous oxide, cuprite (Cu_2O), forms on copper alloys. Copper ions and electrons pass through the film. Copper ions dissolve and precipitate as $\text{Cu}_2(\text{OH})_3\text{Cl}$, independent of alloy chemistry.

Copper alloys are vulnerable to biocorrosion. Differential aeration, selective leaching, underdeposit corrosion and cathodic depolarization have been reported as mechanisms for MIC of copper alloys. Pope et al.¹ proposed that the following microbial products accelerate localized attack: CO_2 ; H_2S ; NH_3 ; organic and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides and disulfides.

In the presence of sulfides, copper alloys form a porous layer of cuprous sulfide with the general stoichiometry Cu_2-xS , $0 < x < 1$. Copper ions migrate through the layer, react with more sulfide, and produce a thick black scale. McNeil and Odom² described a model that predicts sulfide-induced corrosion in the presence of sulfate-reducing bacteria (SRB). Corrosion is initiated by sulfide-rich reducing conditions in the biofilm where the oxide layer is destabilized and acts as a source of metal-containing ions. The authors concluded that if any reaction of metal oxide with sulfide has a high negative standard free energy of reaction, SRB-related MIC will occur. If the reaction has a high positive standard free energy of reaction, this form of corrosion will not occur. Negative standard free energies of reactions were used to predict SRB-MIC for copper alloys. Analysis of sulfide corrosion products recovered from corroding copper alloys confirmed the prediction.

Alloying nickel and small amounts of iron into copper increases resistance to turbulence induced corrosion. Little et al.³ demonstrated dealloying of nickel from 90/10 copper/nickel in association with SRB. SRB are not necessary for MIC-induced pitting of copper alloys. Wagner et al.⁴ described dealloying of nickel in 70/30 copper/nickel exposed to flowing natural seawater (Figure 1). While the role of the biofilm in copper pitting is not entirely clear, it appears that the presence of the biofilm contributes to corrosion by maintaining enhanced local chloride concentrations and differential aeration cells. Pope¹ documented MIC



Figure 1. (a) Biofilm within pits on 70/30 Cu/Ni after 1 month exposure to natural seawater and (b) areas of localized corrosion after removal of biofilm.

of 90/10 copper/nickel, admiralty brass (UNS C44300), aluminum brass (C68700), and welded aluminum bronze at electric generating facilities using fresh or brackish cooling waters. Most of the copper/nickel tubes had underdeposit corrosion due to formation of deposits by slime-forming

organisms in association with iron- and manganese-depositing bacteria. Ammonia-producing bacteria were isolated from scale and organic material on the admiralty brass tubes suffering ammonia-induced stress corrosion cracking. Geesey et al.⁵ demonstrated the role of bacterial exopolymers in corrosion of copper exposed to drinking water.

Nickel Alloys

Nickel alloys are superior to predominantly copper alloys because the protective surface film remains intact under turbulent and erosive conditions. Nickel alloys are used extensively in highly aerated, high velocity seawater applications. Uhlig and coworkers⁶ calculated that a critical nickel concentration of 35% was required for passivity. Nickel alloys containing less than this amount behave like copper. The formation of the protective film on nickel is aided by the presence of iron, aluminum and silicon.

Monel 400 (UNS N04400) is susceptible to pitting and crevice corrosion attack where chlorides penetrate the passive film. Sulfides can cause either a modification or breakdown of the oxide layer. Schumacher⁷ reported that Monel 400 was susceptible to underdeposit corrosion and oxygen concentration cells formed by bacteria. Gouda et al.⁸ demonstrated localized corrosion of Monel 400 tubes exposed in Arabian Gulf seawater where pits developed under deposits of SRB and nickel was selectively dealloyed. Pope¹ reported a case study from nuclear power plants in which severe pitting corrosion associated with dealloying was observed under discrete deposits on Monel heat exchanger tubes. Deposits formed by iron- and manganese-depositing bacteria in association with SRB contained large amounts of iron and copper, significant amounts of manganese and silicon, and reduced amounts of nickel.

Stainless Steels

The corrosion resistance of stainless steels (SS) is due to the formation of a thin passive chromium-iron oxide film at additions of chromium in amounts of 12% or more. Metal-depositing organisms, important in MIC of SS, may catalyze the oxidation of metals, accumulate abiotically oxidized metal precipitates, or derive energy by oxidizing metals. Dense deposits of cells and metal ions create oxygen concentration cells that effectively exclude oxygen from the area

immediately under the deposit. Underdeposit corrosion is important because it initiates a series of events that are, individually or collectively, extremely corrosive. In an oxygenated environment, the area immediately under the deposit becomes a relatively small anode compared to the large surrounding cathode. Cathodic reduction of oxygen may result in an increase in pH of the solution in the vicinity of the metal. The metal will form metal cations at anodic sites. If the metal hydroxide is the thermodynamically stable phase in the solution, metal ions will be hydrolyzed by water with formation of H^+ ions. If cathodic and anodic sites are separated from one another, the pH at the anode will decrease and that at the cathode will increase. The pH within anodic pits depends on specific hydrolysis reactions. The lowest pH values are predicted for alloys containing chromium and molybdenum.

One of the most common forms of MIC attack in austenitic SS is pitting at or adjacent to welds at the heat affected zone, the fusion line, and in the base metal. Borenstein⁹ made the following observations for MIC in 304L (UNS S30403) and 316L (UNS S31603) weldments: both austenite and delta ferrite phases may be susceptible; and varying combinations of filler and base materials have failed, including matching, higher and lower alloyed filler combinations. Microsegregation of chromium and molybdenum with chemically depleted regions increases susceptibility to localized attack.¹⁰

Stainless steels containing 6% or more molybdenum, often called superaustenitic SS, were once thought to be immune to MIC because molybdenum increases resistance to chloride and acid solutions. However, Scott et al.¹¹ documented MIC in laboratory testing of SMO254 (UNS S31254) and AL6X (UNS N08366) SS, both containing 6.5% molybdenum. Little et al.¹² observed deep etching of SMO254 SS after exposure to both an iron/sulfur-oxidizing mesophilic bacterium and a thermophilic mixed SRB culture (Figure 2).

Ennoblement of corrosion potential (E_{corr}) for SS exposed to natural seawater has been reported by several investigators. The practical importance of ennoblement is increased probability of localized corrosion as E_{corr} approaches the pitting potential (E_{pit}) for SS vulnerable to crevice corrosion, especially types 304 (UNS S30400) and 316 (UNS S31600). Sustained ennoblement does not indicate corrosion but persistence of passivity. At the onset of localized corrosion, E_{corr} moves from noble to active regions. Ennoblement has also been reported for SS containing 6% molybdenum and other corrosion-resistant materials.

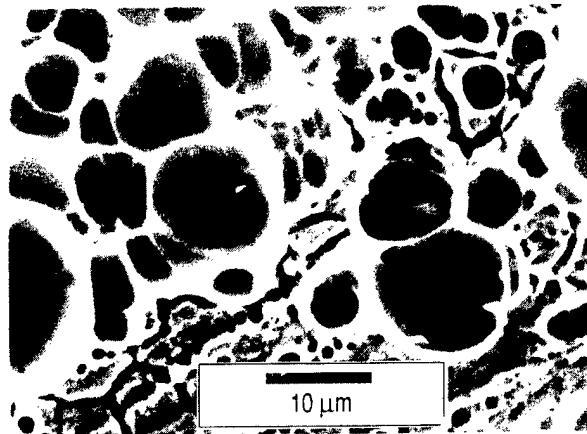


Figure 2. Pitted SMO254 SS after 75-day exposure to mesophilic iron/sulfur-oxidizing bacteria.

Johnsen and Bardal¹³ reported that E_{corr} approached -50 mV (vs. saturated calomel electrode (SCE)) after 28 days for SS that contained 1–3% molybdenum, and 50 – 150 mV (SCE) in the same time period for SS containing 6% molybdenum.

Aluminum and Aluminum Alloys

The corrosion resistance of aluminum and its alloys is due to an aluminum oxide passive film. Anodizing produces thicker insulating films and better corrosion resistance. The natural film on aluminum alloys can be attacked locally by halide ions. The susceptibility of aluminum and its alloys to localized corrosion makes it particularly vulnerable to MIC. Most reports of MIC are for aluminum (99%), 2024 (UNS A92024) and 7075 (UNS A97075) alloys used in aircraft or in underground fuel storage tanks. Localized corrosion attributed to MIC occurs in the water phase of fuel-water mixtures in the bottom of tanks and at the fuel-water interface.¹⁴ Contaminants in fuel include surfactants, water, and water soluble salts that encourage growth of bacteria. Two mechanisms for MIC of aluminum alloys have been documented: production of water soluble organic acids by bacteria and fungi, and formation of differential aeration cells.

Titanium and Titanium Alloys

There are no case histories of MIC for titanium and its alloys. Schutz¹⁵ reviewed mechanisms for MIC and titanium's corrosion behavior under a broad range of conditions. He concluded that at temperatures below 100°C titanium is not vulnerable to iron/sulfur-oxidizing bacteria, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells and hydrogen embrittlement. In laboratory studies, Little et al.¹² did not observe any corrosion of Grade 2 titanium (UNS R50400) in the presence of SRB or iron/sulfur-oxidizing bacteria at mesophilic (23°C) or thermophilic (70°C) temperatures. Using the model of McNeil and Odom² one would predict that titanium would be immune to SRB-induced corrosion. There are no standard free energy reaction data for the formation of a titanium sulfide. If one assumes a hypothetical sulfide product to be titanium sulfide, the standard enthalpy of reaction is +587 kJ. While standard free energies of reaction are not identical to standard enthalpies of reaction, it is still unlikely that titanium will be derivatized to the sulfide under standard conditions of temperature and pressure.

Polymeric Composites

Polymeric composites are subject to many kinds of environmental degradation. Tucker and Brown¹⁶ showed that carbon/polymer composites galvanically coupled to metals are degraded by cathodic reactions in seawater. Jones et al.¹⁷ demonstrated that epoxy and nylon coatings on steel were breached by mixed cultures of marine bacteria. Pendrys¹⁸ reported that p-55 graphite fibers were attacked by a mixed culture of *Pseudomonas aeruginosa* and *Acinetobacter calcoaceticus*, common soil isolates. Possible mechanisms for microbial degradation of polymeric composites include: direct attack of the resin by acids or enzymes, blistering due to gas evolution, enhanced cracking due to calcareous deposits and gas evolution, and polymer destabilization by concentrated chlorides and sulfides.

In laboratory experiments Wagner et al.¹⁹ demonstrated that epoxy resin and carbon fibers, either individually or in composite, were not degraded by sulfur/iron-oxidizing, hydrogen-producing, calcareous-depositing, or SRB. Bacteria colonized resins, fibers and composites, but did not cause damage. SRB preferentially colonized vinyl ester composites at the fiber-resin interfaces and hydrogen-producing bacteria

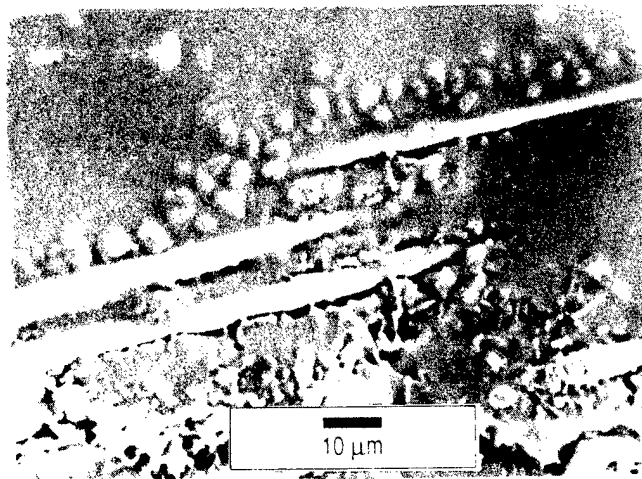
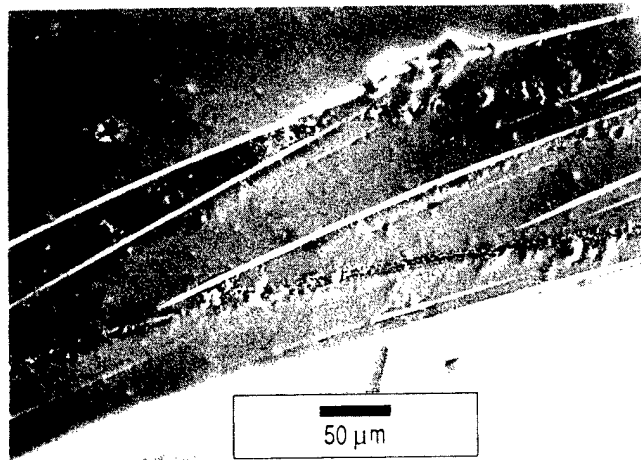


Figure 3. Hydrogen-producing bacteria at disrupted interfaces between fibers and vinyl ester resin.

appeared to disrupt the fiber-vinyl ester resin bonding with penetration of the vinyl ester resin.

Acknowledgments

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